QUANTITATIVE DETERMINATION OF THE FLUID AND INERT COMPONENTS DURING COAL CARBONISATION BY HIGH TEMPERATURE IN-SITU ^{1}H NMR

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Although high temperature in-situ ^{1}H NMR has successfully been used previously to investigate the development of plasticity during coal carbonisation, the proportions of rigid and fluid material have rarely been determined. This has been achieved here using a high temperature Doty NMR probe operating at a frequency of 100 MHz. At maximum fluidity, the mobile phase accounts for up to 45% of the total hydrogen. Indeed, the fluid component increases both in terms of concentration and mobility up to maximum fluidity. Decreasing the particle size below 150 μm suppresses softening, but at maximum fluidity, the concentration of inert component is independent of the particle size.

INTRODUCTION

Although standard empirical tests such as Gieseler plastometer and Audibert-Arnu dilatometer are widely used to ascertain the plasticity behaviour of coking coals [1], these tests do not easily relate to the actual structural changes that occur. High temperature in-situ ^{1}H NMR has successfully been used to investigate the motion of coals in-situ during carbonisation, where parameters reflecting the spin-spin relaxation times T_2s, have been correlated with plasticity [2]. There are usually two contributions to the ^{1}H NMR signals of coals: a mobile component with a Lorentzian decay, and an inert component with a Gaussian distribution [3]. Coal being a macromolecular network contains a substantial inert component which does not soften and forms the broad constituent of the NMR signal.

In the late 70's, Sanada and coworkers conducted the first high temperature ^{1}H NMR study on coal and pitches at the early stages of carbonisation [4]. The development of plasticity in coals was monitored by changes in the half width of the spectra. However, due to experimental factors including the relatively small sample size and low magnetic field used (37.5 MHz for ^{1}H), the spectra could not be deconvoluted to derive the proportion of inert material present. This limitation was overcome from 1983 onwards by Lynch et al [2,3,5,6], who have referred to the technique as "Proton Magnetic Resonance Thermal Analysis" (PMRTA). They have used mainly the empirical parameter, M2t16, corresponding to the spectrum truncated at 16 kHz which was found to be the optimum frequency for gauging changes in fluidity [6]. However, in-situ ^{1}H NMR has not been used widely to determine the overall concentrations of fluid and inert material during coal carbonisation, due to the possiblity of truncating broad Gaussian signals when signal to noise levels tend to be low at high temperatures. This has been achieved here using a high temperature Doty NMR probe operating at a frequency of 100 MHz. Three Australian bituminous coals with different plastic properties have been investigated and both the oncentration and mobility of the fluid components have been monitored. Furthermore, for one of the coals investigated the effect of the particle size has been studied for fractions below 212 μm.

EXPERIMENTAL

Table 1 lists the proximate and maceral analysis as well as the Gieseler plastometer results for the three coals investigated. The coals were ground to -212 μm. Sample AUS-1 was also ground to give <45 and 212-45 μm fractions.

In the high temperature measurements, the 90° pulse width varied with temperature between 2.2 μs at ambient to 3.0 μs at 600°C. The solid echo pulse sequence (90° - τ - 90°) with a refocusing of 5 μs was used in order to minimise the loss of signal due to the dead time of the NMR coil. About 40-70 mg of sample was packed in a zirconia container which was placed horizontally in the stator. A flow of 12 dm^3 min^{-1} of dry nitrogen was used to transfer heat to the samples and to remove the volatiles escaping trough a small ventilation hole in the container. Spectra were obtained at a number of different temperatures and the free induction decays (FIDs) were transferred from the spectrometer to a PC for processing and fitted to Lorentzian and Gaussian components, as appropriate. The spectra obtained in the fluidity range could best be fitted to either one Gaussian and one Lorentzian component or two Gaussian components.

RESULTS AND DISCUSSION

General aspects Figure 1 shows the ^1H NMR spectra for sample AUS-1 obtained at 25°C, 453°C - maximum fluidity and 529°C - after resolidification. Figure 2 compares the peak widths at half height, $\Delta H_{1/2}$, measured in-situ at temperatures up to 600°C for the three coals and Figure 3 shows the deconvoluted spectra for two of the coals at the temperature of maximum fluidity. The coals behave in a similar way with a constant $\Delta H_{1/2}$ corresponding to single Gaussian component before the onset of thermoplasticity (300-350°C). The maximum fluidity at 430-480°C is reflected by the minimum in $\Delta H_{1/2}$, corresponding to a maximum in T_2. During the fluidity range, the peak width of the plastic phase is only between 20 and 30% of that for the initial coal. Comparable observations in peak half width have been reported earlier by Sanada [4,7] and by Lynch et al. Using the M_{2T16} parameter [5,6]. As expected, the fluid component has its highest contribution to the total NMR signal at maximum fluidity.

After the onset of resolidification, (470-510°C) the average peak width increases to reach a value similar to that of the initial coal with only a single Gaussian component being observed. The inert component represented by a Gaussian distribution has a relativerly constant T_2 of ≈20 μs throughout the temperature range studied (Table 2).

Proportions of rigid and fluid material For the coals investigated, Table 2 lists the proportions of these components at maximum fluidity and their associated spin-spin relaxation times (T_2s). The data (<212 μ fractions indicate that the extent of fluidity development for AUS-4 is much less than for AUS-1 and AUS-8 (Table 2). It generates a lower concentration of fluid material that has considerably less mobility than that for the other coals (Table 2). Indeed, the spectrum at maximum fluidity for AUS-4 can be fitted using only two Gaussian components, without including the Lorentzian for the most fluid material. Further, Figure 2 indicates that maximum fluidity is attained at a lower temperature for AUS-1 and AUS-8 than AUS-4, consistent with the Gieseler plastometer data. For AUS-8, the concentration of inert material only accounts for 56% of the total hydrogen observed (Table 2).

Figure 4 shows the evolution of the fluid component for sample AUS-1. During the plastic stage, the T_2 or mobility of the Lorentzian component increases, together with its contribution to the total signal. This reaches a maximum at 450°C and then decreases during the resolidification process. Thus, the

development of fluidity and subsequent resolidification in the coals follow the same trend involving changes in both concentration and mobility of the plastic phase.

Particle size For AUS-1, the particle size has a significant effect on the development of fluidity. Table 3 lists the proportions of rigid and mobile material and their T_2s at maximum fluidity for the three different particle size fractions studied. The mobility of the narrowest component is suppressed for the <45μm fraction, and there is still a noticeable difference between the <212 and 212-45 μm fractions. The suppression of fluidity with decreasing particle size is represented by a reduction in the mobility of the fluid material, rather than a reduction in its concentration. This reduction in fluidity may be ascribed to either an oxidation effect or a combination of reduced voidage between the coal particles and the fact that fluid material will escape easier from smaller particles. Careful grinding of the coal and high temperature NMR analysis of the resultant fractions strongly suggests that the latter is the prime cause of the fluidity loss. Furthermore, it has been shown that fluidity is essentially a reversible phenomenon provided that the sample is cooled rapidly from the temperature of maximum fluidity.

CONCLUSIONS

The results have confirmed the ability of high temperature ^{1}H NMR to follow coal carbonisation in-situ. The approach used here is able to describe the carbonisation process in terms of the proportions of rigid and fluid material as well as the mobility of the latter. Decreasing the particle size below 150 μm suppresses softening, but at maximum fluidity, the proportion of inert material is independent of the particle size.

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Table 1 Proximate analysis, vitrinite reflectance, atomic H/C and temperature of maximum fluidity determined by Gieseler and NMR for the coals investigated.

	VM (db)	Ro (max)	atomic H/C	Tem. max / °C
AUS-1	23.1	1.20	0.60	451 (453) [a]
AUS-4	19.63	1.46	0.61	472 (470)
AUS-8	33.94	0.86	0.74	460 (460)

[a] Values in brackets were determined by ^{1}H NMR.

Table 2 Deconvolution into two components identified in the ^{1}H NMR spectra obtained at maximum fluidity for the three coals investigated.

	% rigid	T_2 rigid / μs	% mobile	T_2 mobile / μs
AUS-1*	62	20.7	38	82
AUS-4**	81	20.9	19	68
AUS-8*	56	22.2	44	92

* Deconvoluted into one Gaussian and one Lorentzian components.

** Deconvoluted into two Gaussian components.

Table 3 Deconvolution into two components of the ^{1}H NMR spectra obtained at maximum fluidity for AUS-1 as a function of the particle size.

	%rigid	T_2 rigid / μs	% mobile	T_2 mobile / μs
<45μm	63	18.5	37	48
<212μm	62	20.7	38	82
45μm - 212μm	68	23.3	32	111

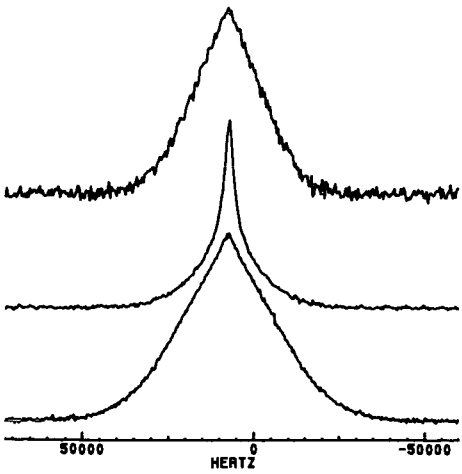

Figure 1 ^{1}H NMR spectra for AUS-1 at 25°C (bottom), maximum fluidity at 453°C (middle), and resolidification at 529°C (top).

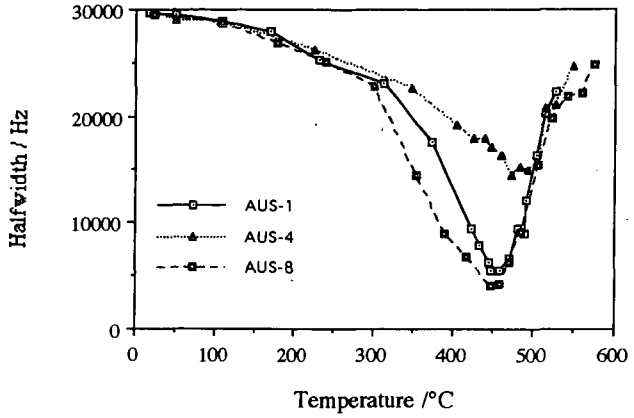

Figure 2 Variation in the average peak half-width for the three coals investigated (<212 μm). The peak half-width is dominated by the contribution from the mobile component close to maximium fluidity.

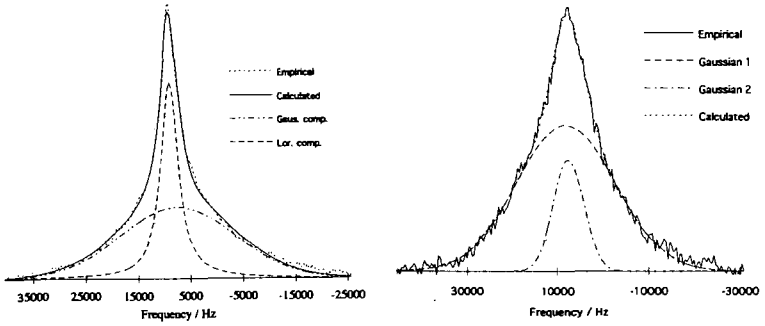

Figure 3 Deconvoluted ^1H NMR spectra at maximum fluidity for AUS-1 (rigth), and AUS-4 (left).

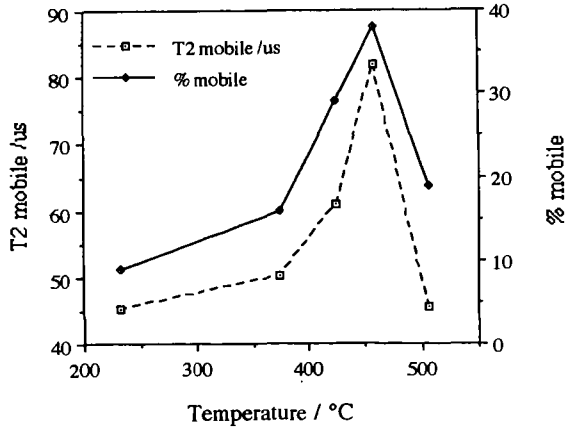

Figure 4 Evolution of the fluid component for AUS-1 with temperature.